Second preliminary draft

Lade 5778

JUN 1 2 1963

79179

MASTER

Vibrational Assignment and Force Constants of S_8 from a Normal-Coordinate Treatment

D. W. Scott and J. P. McCullough

Bartlesville Petroleum Research Center, Bureau of Mines, U. S. Department of the Interior, Bartlesville, Oklahoma*

---

*Contribution No.   from the thermodynamics laboratory. This investigation was part of American Petroleum Institute Research Project 48A on "Production, Isolation, and Purification of Sulfur Compounds and Measurement of Their Properties," which the Bureau of Mines conducts at Bartlesville, Oklahoma and Laramie, Wyoming.

F. H. Kruse

Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico†

---

† Some of this work was performed under the auspices of the U. S. Atomic Energy Commission.

(ABSTRACT)

Normal-coordinate calculations for S_8 were revised by use of new far-infrared spectral data and a more elaborate potential function. Representation of the observed frequencies required that the basic Urey-Bradley field be supplemented with an extra quadratic cross-term between adjacent S—S bonds.

This paper was submitted for publication in the open literature at least 4 months prior to the issuance date of this Microcard. Since the U.S.A.E.C. has no evidence that it has been published, the paper is being distributed in Microcard form as a preprint.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

Facsimile Price $ 1.60
Microfilm Price $ .80
Available from the
Office of Technical Services
Department of Commerce
Washington 25, D. C.

(TEXT)

A paper of the same title by two of the present authors (1) reported a normal-coordinate treatment of S_8 that took account of torsional forces and gave a vibrational assignment consistent with thermodynamic data. The reasons for revision of the earlier treatment are threefold: (a) Reinvestigation of the far-infrared spectrum, reported in the Experimental section, showed that the low infrared-active fundamentals are 191 and 243 cm.$^{-1}$ instead of 150 and 225 cm.$^{-1}$, as inferred from the earlier work of Barnes (2); (b) Availability of digital-computer methods allowed a more thorough investigation of the molecular force field than was possible with the desk-calculator methods used earlier; (c) Thermodynamically significant shifts of low frequencies between vapor and condensed phases have been observed for other molecules (3); such observations suggested caution in use of condensed-state frequencies of S_8 for comparisons involving the vapor-state thermodynamic properties.

CALCULATIONS AND DISCUSSION

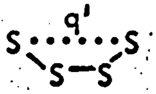
The numerical calculations reported here were done with an IBM 7090 computer and used G-Matrix Evaluation Program SD-9064-I, Z-Matrix Evaluation Program SD-9080-I, and Vibrational Secular Equation Programs SD-9032-I and -IV, all kindly supplied by Dr. J. H. Schachtschneider of Shell Development Company. Molecular structure parameters (S—S distance, 2.048 A; S—S—S angle, 107° 54') were taken from the work of Caron and Donohue (4) on orthorhombic sulfur.

Of various force fields investigated, the one that was found to give satisfactory agreement between observed and calculated frequencies is:

$$\begin{aligned} 2V = {} & \sum^{8} K(\Delta r)^2 + 2\sum^{8} K' r\Delta r + \sum^{8} H(r\Delta\phi)^2 + 2\sum^{8} H' r(r\Delta\phi) + \\ & \sum^{8} F(\Delta q)^2 + 2\sum^{8} F' q\Delta q + \sum^{8} C(\Delta q')^2 + 2\sum^{8} C' q'(\Delta q') + \\ & \sum^{8} Y(r\Delta\tau)^2 + 2\sum^{8} Y' r(r\Delta\tau) + 2\sum^{8} P\Delta r\Delta r'. \end{aligned}$$

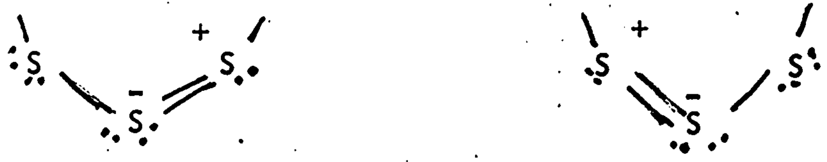
The internal coordinates are the changes in the bonded S_i—S_{i+1} and S_{i+1}—S_{i+2} distances r and r', non-bonded $S_i\cdots S_{i+2}$ and $S_i\cdots S_{i+3}$ distances q and q', S-S-S angle ϕ, and torsional angle of the S-S-S-S group τ. The constants K', H', and Y' were eliminated in the removal of redundant coordinates, and the constants F' and C' were constrained by the conventional assumptions, $F' = -0.1\,F$ and $C' = -0.1\,C$. Terms in the potential energy involving the constant F were retained only if they involved internal coordinates of the "gem" configuration

and terms involving C only if they involved internal coordinates of the "cis" configuration



These approximations (and neglect of non-bonded $S_i \cdots S_{i+4}$ interactions) were computational expedients made because the Z-matrix program had no provision for non-bonded interactions between ends of chains of 5, 6, or 7 atoms.

The six constants not eliminated or constrained were adjusted to give a least squares fit of the calculated frequencies to the observed frequencies, weighted on an absolute basis. The five constants, $\underline{K}$, $\underline{H}$, $\underline{F}$, $\underline{C}$, and $\underline{Y}$, pertain to the basic Urey-Bradley field, except as modified by the approximations just mentioned. The sixth constant, $\underline{P}$, is a specific interaction constant that may have its physical basis in contributions to the normal state of the molecule from structures with a 3$\underline{d}$ orbital used for bonding.



Stretching of one bond would favor the structure with the neighboring bond double, so that more potential energy would be required to stretch the second bond simultaneously.

The results of the calculations are summarized in Table I, which gives a comparison of observed and calculated wave numbers, and also the potential energy distribution and the final converged values of force constants with their uncertainty. In the selection of observed wave numbers, the spectra of solutions were given preference over the spectra of crystals, as more nearly representing the free molecule. The

TABLE I

Summary of Normal Coordinate Calculations for S_8[a]

	obs ν	calc ν	$\Delta\nu$	$\underline{K}$	$\underline{H}$	$\underline{F}$	$\underline{C}$	$\underline{Y}$	$\underline{P}$
$\underline{a}_1$	475	473	2	61	4	9	2	3	20
	218	214	4		22	59	4	14	
$\underline{b}_1$	411	411	0	153		-3	1	1	-51
$\underline{b}_2$	243	241	2		27	67	6		
$\underline{e}_1$	471	473	-2	69	3	11	1		16
	191	195	-4		22	52	-1	27	
$\underline{e}_2$	(475)[b]	475	0	88	1	10		1	
	152	149	3	1	24	56	18	1	
	86	83	3	2	2	4	15	77	
$\underline{e}_3$	437	437	0	126		4			-30
	(218)[b]	223	-5	2	22	51	17	9	
Force constant (md/A)				1.868	0.051	0.312	0.037	0.024	0.311
Uncertainty				.022	.026	.060	.010	.003	.013

[a] Observed and calculated wave numbers (in cm^{-1}) of the fundamental vibrations and their differences, the potential energy distribution (entries rounded to nearest %), and final converged values of force constants with their uncertainty.

[b] Assumed coincidence.

normal modes, expressed as Cartesian displacement coordinates, are illustrated in Figure 1. The consistency of the assignment of Table I with the observed spectra is shown in Table II. There, in addition to the far-infrared data of this research, are listed published data from various sources (5—12). In the range of fundamentals and binary combinations, all but a few very weak and doubtful features of the observed spectra are accounted for by the assignment proposed here. This assignment includes the value 411 cm^{-1} for the inactive $\underline{b}_1$ fundamental deduced by Neff and Walnut (12) from the temperature dependence of intensity of the 845 cm^{-1} infrared band of the crystals. An $\underline{e}_2$ fundamental is assumed to coincide with 475 cm^{-1} ($\underline{a}_1$) and an $\underline{e}_3$ fundamental with 218 cm^{-1} ($\underline{a}_1$). Such coincidences were shown to be likely by preliminary calculations that did not include the highest $\underline{e}_2$ and lowest $\underline{e}_3$ fundamentals in the list of observed frequencies used for adjusting the force constants.

Past difficulties in making a vibrational assignment for S_8 are understandable now. Because of the two coincidences, the Raman-active fundamentals are not all observed separately. Moreover, in the Raman spectra of the condensed phases, there are weak bands (184 and 248 cm^{-1}) from fundamentals forbidden by the strict vapor-state selection rules. The breakdown of selection rules in the condensed phases could not be recognized as such until the lower two infrared active fundamentals were determined accurately and found to have nearly the same wave numbers as the weak Raman bands.

TABLE II

Spectra of S_8 and Interpretation[a]

Raman, cm^{-1}		Infrared, cm^{-1}		Interpretation
Crystals	Solution	Crystals	Solution	
49 s				lattice
85 s	86 s(d)			e_2 fundamental
114 w				lattice
152 s	152 s(d)			e_2 fundamental
184^b w	184^b w		191^c s	e_1 fundamental
216 s	218 s(p)			a_1 (& e_3) fundamental
243^b w	248^b w		243^c s	b_2 fundamental
	299 w			2 x 152 = 304 $A_1 + B_1 + B_2$
	334 w ?			86 + 243 = 329 E_2
434 m	437 w(d)	435^b w		e_3 fundamental
		465 s	471^c m	e_1 fundamental
470 s	475 s(p)			a_1 (& e_2) fundamental
		509 w	520^c vw	86 + 437 = 523 $E_1 + E_3$
		549 w	546^c w	86 + 475 (e_2) = 561 $A_1 + A_2 + B_1 + B_2$
			575^c vw	?
	591 vw	584 w	591^c w	152 + 437 = 589 $E_1 + E_3$
		618 w	621^c w	152 + 475 (e_2) = 627 $A_1 + A_2 + B_1 + B_2$
		659 w	665^c w	191 + 475 = 666 E_1
		679 w (E_1 ?)	686 w	243 + 437 = 680 E_1
		711 w (E_1)	714 w	243 + 475 = 718 B_2
		845 m (E_1)	854 m	411 + 437 = 848 E_1
		873 vw (B_2 ?)		?
		903 w (B_2)	912 w	437 + 471 = 908 $B_1 + B_2 + E_2$
		936 w (B_2, E_1)	942 w	471 + 475 = 946 E_1

Region above 950 cm^{-1} omitted.

[a] Abbreviations: s, strong; m, medium; w, weak; vw, very weak; (p) polarized; (d), depolarized; (B_2) and (E_1), species of infrared band indicated by effects of orientation or polarized radiation.

[b] Appearance in violation of strict vapor-state selection rules.

[c] Observed in this research; other values from literature.

The present vibrational assignment differs from the assignment of the earlier paper (1) by increases in four fundamentals (400 to 411, 225 to 243, 150 to 191, and 184 to 218 cm^{-1}, the last two doubly degenerate). These changes are enough to destroy the consistency with thermodynamic data demonstrated for the earlier assignment, i.e., with the present assignment, values of $\Delta \underline{H}°_0$ for the reaction, $8S(c, rhombic) = S_8(g)$, calculated from vapor pressure data, shows a distinct trend with the temperature of the vapor pressure determination. However, the test for thermodynamic consistency implies that the vapor-state frequencies are identical with the condensed-phase frequencies on which the assignment is based and, in addition, that the vibrations are harmonic. It is known that low-frequency vibrations may have lower frequencies in the vapor state than in a condensed state (3); it might be expected then that low frequencies of S_8, particularly the lowest $\underline{e}_2$ frequency, are lower in the vapor state than in crystals or solution. Also, if the lowest $\underline{e}_2$ mode is appreciably anharmonic, the observed 86 cm^{-1} Raman band includes a superposition of "hot bands," and the fundamental, even in the condensed states, may have a wave number significantly different from 86 cm^{-1}. If all the burden of providing consistency with thermodynamic data is placed on the lowest $\underline{e}_2$ mode, then, if harmonic, it must be about 60 cm^{-1} in the vapor state instead of 86 cm^{-1}. Determination of the vapor-state molecular spectra of S_8 presents the formidable difficulties of the high boiling point of sulfur (444.6°C.) and the existence of a complex mixture of other species besides S_8 in the vapor. Considerable time may elapse before the foregoing suppositions are put to the test of experiment. In the interim, it is suggested that calculations of vapor-state thermodynamic functions of S_8 to the harmonic-oscillator approximation be made with the vibrational assignment of this research except that 60 cm^{-1} instead of 86 cm^{-1} be used for the lowest $\underline{e}_2$ mode.

Attempts to draw conclusions about the barrier to internal rotation about the S—S bonds in the free S_8 molecule from the values of the force constants $\underline{Y}$ and $\underline{C}$ in Table I should be done with caution, because these force constants apply strictly to the molecule in a condensed phase and include contributions to the force field from neighboring molecules.

EXPERIMENTAL

The far-infrared spectrum of solutions of rhombic sulfur was determined between 50 and 670 cm^{-1} with the results shown in Figure 2, which includes the pertinent experimental details.

REFERENCES

1. D. W. Scott and J. P. McCullough, J. Mol. Spectroscopy, 6, 372 (1961).
2. R. B. Barnes, Phys. Rev., 39, 570 (1932).
3. D. W. Scott, G. B. Guthrie, J. F. Messerly, S. S. Todd, W. T. Berg, I. A. Hossenlopp, and J. P. McCullough, J. Phys. Chem., 66, 911 (1962).
4. A. Caron and J. Donohue, Acta Crystallographica, 14, 548 (1961).
5. P. Krishnamurti, Ind. J. Phys., 5, 105 (1930).

6. C. S. Venkateswaran, Proc. Ind. Acad. Sci., 4A, 345, 414 (1936).
7. K. Venkateswarlu, Proc. Ind. Acad. Sci., 12A, 453 (1940).
8. R. Norris, Proc. Ind. Acad. Sci., 13A, 291 (1941), ibid., 16A, 287 (1942).
9. H. Gerding and R. Westrik, Rec. Trav. Chim., 62, 68 (1943).
10. H. J. Bernstein and J. Powling, J. Chem. Phys., 18, 1018 (1950).
11. G. M. Barrow, J. Chem. Phys., 21, 219 (1953).
12. V. D. Neff and T. H. Walnut, J. Chem. Phys., 35, 1723 (1961).

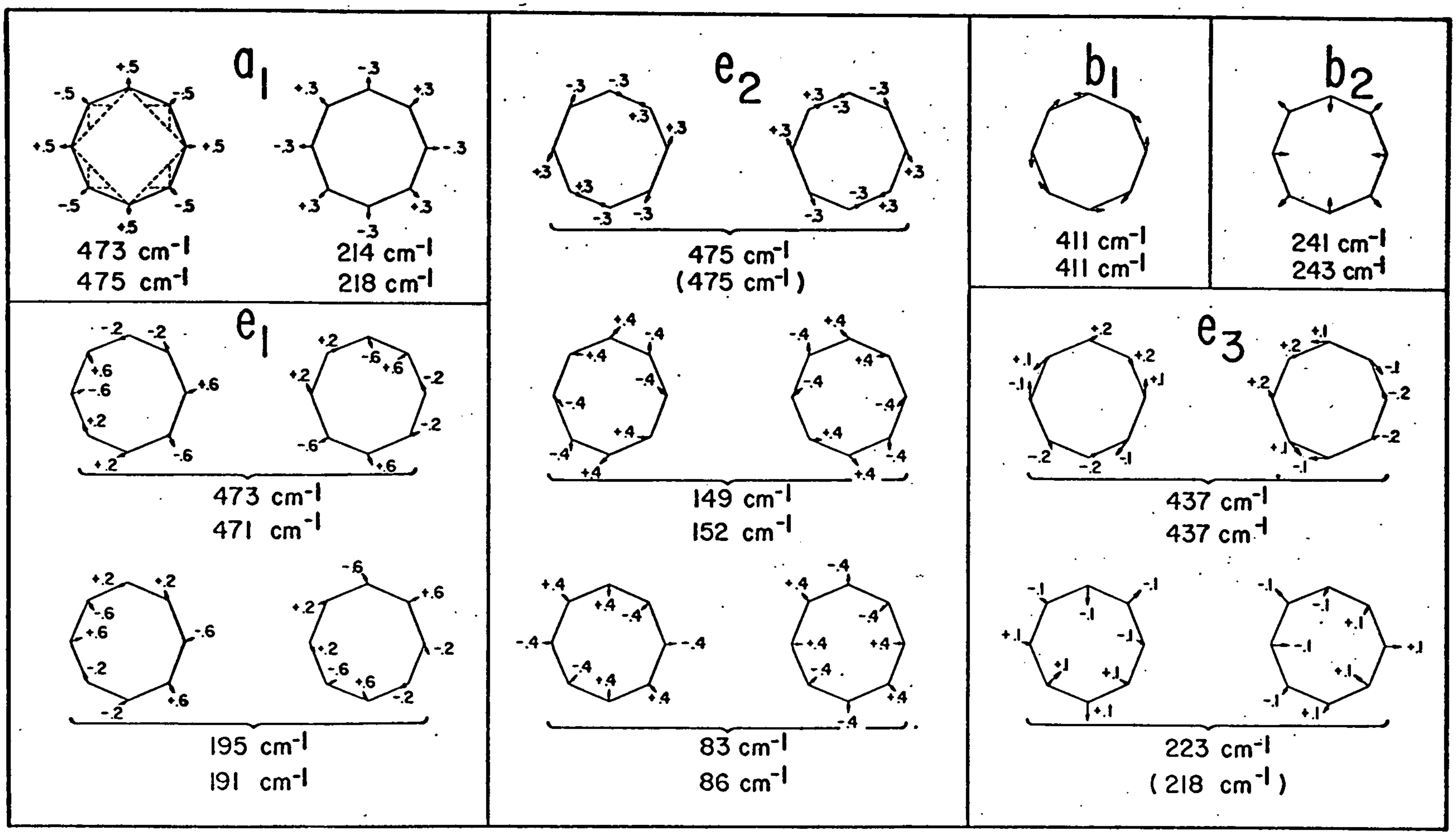
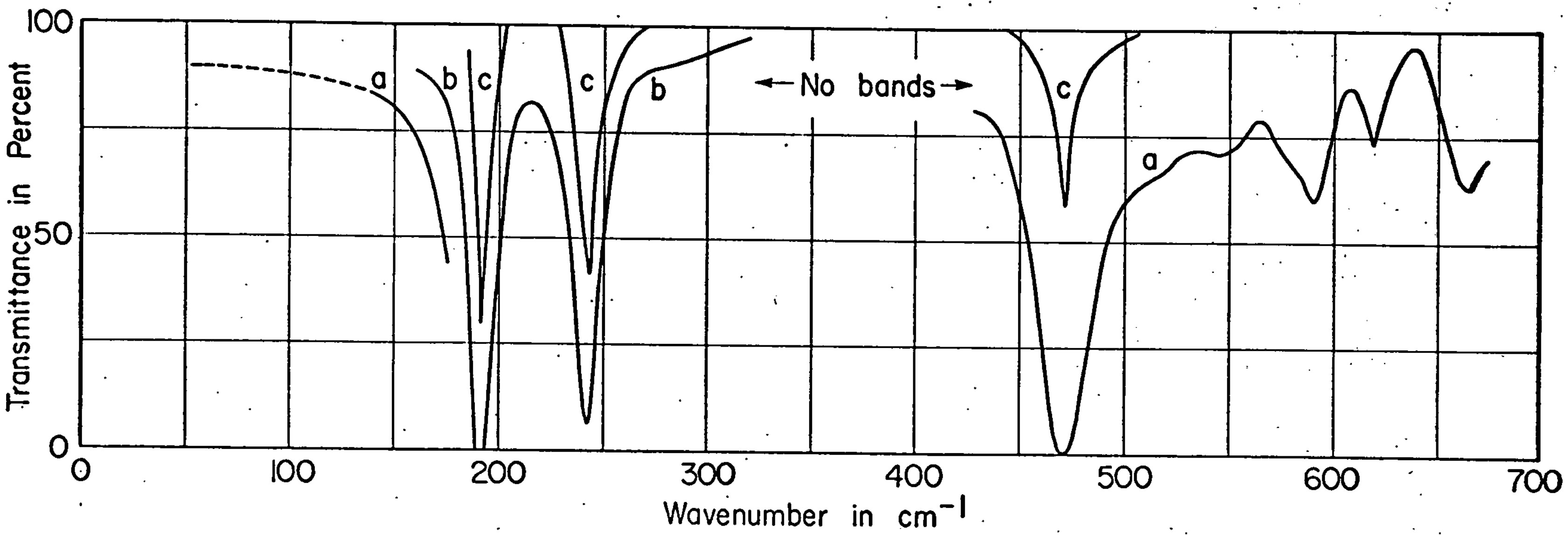
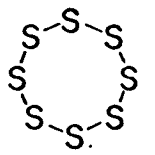


Fig. 2. Normal modes of S_8 expressed in Cartesian displacement coordinates in A per (change in normal coordinate) x 10. Numbers at heads of arrows denote components perpendicular to plane of paper, rounded to one significant digit. Atoms at 3, 6, 9 and 12 o'clock above plane of paper; atoms at 1:30, 4:30, 7:30 and 10:30 below plane of paper. Upper number calculated, lower number from wave numbers.





COMPOUND OCTATOMIC SULFUR S_8	SOURCE & PURITY GULF SULFUR FELLOWSHIP, MELLON INSTITUTE	STATE: SOLUTION TEMPERATURE: ROOM CELL LENGTH: 3.2mm	a: IN CS_2 (SAT.) b: DILUTED 1:9 c: IN BENZENE (SAT.) INSTRUMENT: P-E 301

Fig. 2. Far-infrared spectrum of S_8.

Second preliminary draft
Ladc 5778

JUN 1 2 1963

78179

MASTER

Vibrational Assignment and Force Constants of S_8 From a Normal-Coordinate Treatment

D. W. Scott and J. P. McCullough

Bartlesville Petroleum Research Center, Bureau of Mines, U. S. Department of the Interior, Bartlesville, Oklahoma[*]

---

[*] Contribution No. from the thermodynamics laboratory. This investigation was part of American Petroleum Institute Research Project 48A on "Production, Isolation, and Purification of Sulfur Compounds and Measurement of Their Properties," which the Bureau of Mines conducts at Bartlesville, Oklahoma and Laramie, Wyoming.

F. H. Kruse

Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico[†]

[†] Some of this work was performed under the auspices of the U. S. Atomic Energy Commission.

(ABSTRACT)

Normal-coordinate calculations for S_8 were revised by use of new far-infrared spectral data and a more elaborate potential function. Representation of the observed frequencies required that the basic Urey-Bradley field be supplemented with an extra quadratic cross-term between adjacent S—S bonds.

This paper was submitted for p
in the open literature at least 9
prior to the issuance date of thi
card. Since the U.S.A.E.C. has
dence that it has been publishe
per is being distributed in Mic
form as a preprint.

Facsimile Price $ 1.10
Microfilm Price $ .80

Available from the
Office of Technical Services
Department of Commerce
Washington 25, D. C.